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Isotopenpraxis 26 (1990) 3, pp. 118–121

Simple Thermochromatographic Separation of ^{67}Ga from Metallic Zinc Targets

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Dedicated to Professor Dr. rer. nat. habil. R. Münze on the occasion of his 60th birthday on March 1st, 1990

An experimental realization of the vacuum thermochromatographic separation of ^{67}Ga from metallic zinc targets is described. High yields of the radionuclide ^{67}Ga with low zinc contaminations are demonstrated. Results are discussed with respect to expected data from theoretical considerations.

Es wird eine experimentelle Realisierung der vakuum-thermochromatografischen Trennung des Kernreaktionsproduktes ^{67}Ga von metallischen Zink-Targets dargestellt, die auf dem Konzept selektiver thermischer Desorptionen der Metalle von metallischen Adsorbensoberflächen beruht. Bei Analyse der experimentellen Daten werden hohe Ausbeuten des Radionuklides ^{67}Ga mit geringsten Zink-Kontaminationen festgestellt. Die Ergebnisse werden im Vergleich zu den aus theoretischen Betrachtungen zu erwartenden Werten diskutiert.

Keywords

gallium; gallium 67; isotope production, processes; separation; thermochromatography; zinc

1. Introduction

The ^{67}Ga is applied in nuclear medicine in cancer diagnosis. It is usually produced by proton or deuteron irradiation of metallic zinc targets. In these reactions enriched zinc (^{67}Zn, ^{68}Zn) is often preferred [1–4]. In such cases the irradiation and separation techniques have to guarantee either the routine recycling of one and the same target [5–8] or regeneration of the target material. For separating of ^{67}Ga from the target material common solvent extraction processes are applied.

Our experience in handling high-temperature techniques for radioisotope separations stimulated us to investigate the thermochromatographic separation of nuclear reaction products and target metals. Recently, vacuum and gas thermochromatographic separation techniques have been described by *Novgorodov* et al. for the separation of ^{111}In from natural Ag matrix and of ^{111}In from Sn targets [6,7].

With the example of the pair ^{67}Ga/^{nat}Zn we try to demonstrate here a special version of thermochromatographic separation techniques. The method is based on the thermic release of the macrocomponent zinc, whereas the radionuclide ^{67}Ga is completely adsorbed on a metallic surface.

2. Experimental

^{67}Ga: Nuclear reaction ^{nat}Zn(d, xn)^{67}Ga has been used for the production of ^{67}Ga at the U-120-cyclotron of the CINR Rossendorf, GDR. Natural zinc foil, weight 2–3 g, thickness 2 mm, was used as target material. Irradiation parameters were as follow: e_d = 13.5 MeV, I_d = 50μA, T = 10 h. The yield of ^{67}Ga was of 200 MBq.

Vacuum thermochromatography: The vacuum thermochromatographic experiments were carried out at the Laboratory of Nuclear Problems, JINR Dubna, USSR. Details of the vacuum thermochromatography equipment are published in refs. [6, 7]. First studies on thermochromatographic separation of the system Ga/Zn were carried out in a quartz tube of diameter 5 mm and length 400 mm, closed at one end. The irradiated zinc (5 mg) was situated at the closed end, the open end was connected to the vacuum apparatus. For the experiments the vacuum applied was $7 \cdot 10^{-5}$ Pa.

In a second step of the investigations the irradiated zinc was enveloped with an adsorbent metal foil and the packet was treated within the quartz tube as described is the case of absence of adsorbent metals.

The final step of the studies was to build up a simple technological version of the separation process.

In the first experiments amounts of 2–5 mg irradiated zinc were used. In the last step 2–3 g of the target were applied.

For quantitative determination of gallium and zinc amounts the main γ-rays of ^{67}Ga (184.6 keV, 300.2 keV) and ^{65}Zn (1115.5 keV) were analysed using Ge(Li)- and NaI(Tl)-detectors. The nuclear decay data were taken from ref. [9].

3. Results

In the first separation experiments with and without adsorbent metals (20 µm thick foil of tantal was choosen) the temperature was raised slowly up to 1010 (10) K within 100 minutes. At 720 K the distillation of the macrocomponent Zn began, detected by a slow decrease of the ^{65}Zn radioactivity measured at the original position of the target metal in the quartz tube.

The amount of the target material zinc, remaining at the start point of the quartz tube or within the tantal envelope, was about 0.4%. The released zinc is distributed along the quartz tube commonsurate with the temperature of the quartz surface. The maximum of adsorbtion lies at T_a = 550 (20) K, Fig. 1.

The radionuclide ^{67}Ga remains almost quantitatively at the original place inside the quartz tube and also inside the tantal casing. In the latter case, only 2.5% of this isotope is released and adsorbed immediately beside the Ta container.

However, whereas the ^{67}Ga is localized at the hot quartz surface in a chemicaly-complicated way and is not easy to separate from this surface, on Ta-surfaces the ^{67}Ga is adsorbed in its metallic form.

In a following study the kinetics of the temperature release of Ga and Zn isotopes were investigated. The temperature of the tantal envelope was regulated up to a constant value, where the release of the radioisotopes is significant. The results of these measurements are illustrated in Figs. 2, 3 for zinc (T = 780 K) and Ga (T = 1370 K), respectively.

From the Figs. 2, 3 the temperature release of gallium and zinc depending on the temperature applied and the heating period can be derived quantitatively. The parameter of interest is the half time $t_{0.5}$ of the temperature release of ^{67}Ga at a given temperature.

For the macro-component zinc this half time of release is $t_{0.5}$ = 30 (5) minutes at T = 780 (10) K. The velocity of this process can be regulated by selection of the release temperature. For example, at temperatures of 900 – 1000 K more than 93% of the target material zinc are separated from tantal within a few minutes. On the other hand, losses of the tracer component ^{67}Ga are depressed because of the adsorption of this radioisotope on the Ta surface. Desorption of ^{67}Ga from the tantal surface starts at temperatures higher than

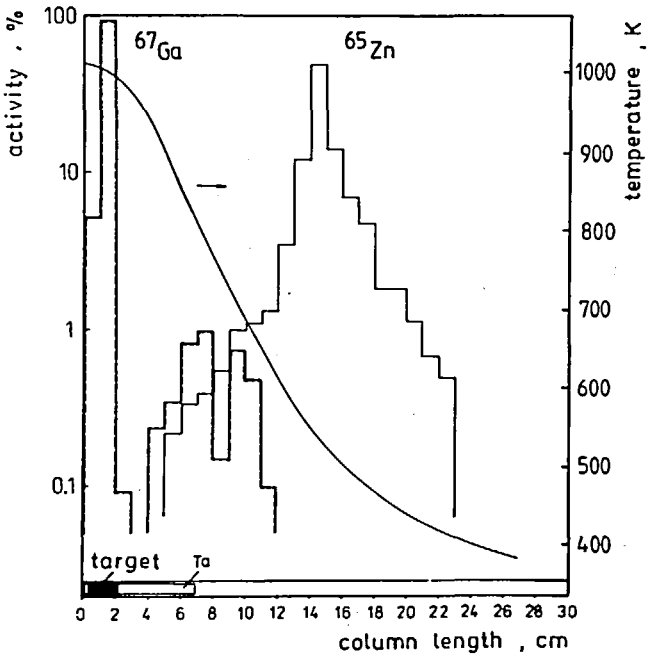

Fig. 1. Thermochromatogram of ^{65}Zn and ^{67}Ga along a quartz surface after thermic release of the zinc target out of the tantal envelope
($p = 7 \cdot 10^{-5}$ Pa, T_{max} = 1010 K, t = 100 min, m_{Zn} = 2.5 g)

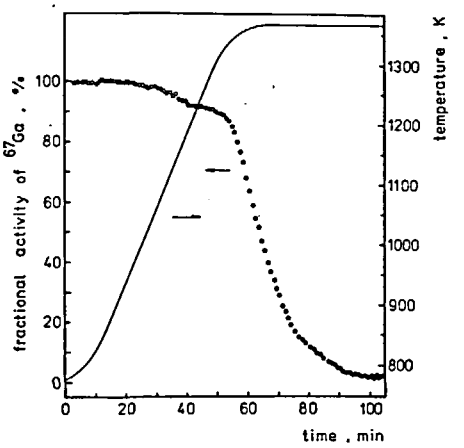

Fig. 2. Thermic release of metallic zinc enveloped in tantal foil
($p = 7 \cdot 10^{-5}$Pa, T_{max} = 780 K, m_{Zn} = 2.5 g)

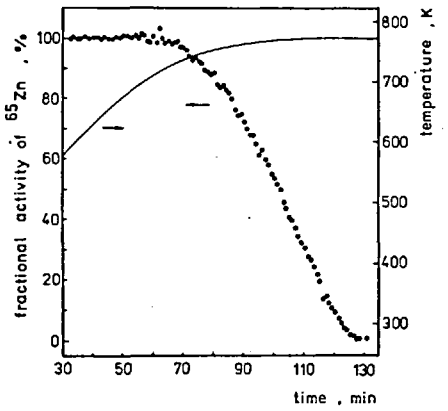

Fig. 3. Thermic release of ^{67}Ga from tantal surfaces
($p = 7 \cdot 10^{-5}$ Pa, T_{max} = 1370 K)

1200 K. For parameters of T = 1370 (10) K = constant, the half time of temperature release of the ^{67}Ga is found to be $t_{0.5}$ = 15 (2) minutes; Fig. 3.

One practicable realization of this separation is based on the idea of a metallic adsorbent container, holding the irradiated target, and a quartz facility, acting later as the place of the adsorption of the released target metal. The radionuclide of interest remains in the container. Fig. 4 shows a schematic view of the tantal container used in the experiments. The lid is easy to handle and shows a lot of additional surfaces for the adsorption of ^{67}Ga as well as pores for the passage of the volatile zinc. The irradiated zinc (2 – 3 g) is put into the container. Then it is closed and cut down into the vertical quartz facility, 400 mm long and with a diameter matching that of the Ta container. The tube is closed at the bottom, connected with the vacuum pump at the top, and surrounded by an electric oven at the position of the Ta container.

Experimental values of temperature and heating period were so chosen, that the main amount of the target material is released at temperatures of 710 (10), 720 (10) and 780 (10) K within a period of 150, 100 and 100 minutes, respectively. After these periods the container is decontaminated from residues of zinc during a second one-hour heating period at higher temperatures of 820 (10), 940 (10) and 1080 (10) K, respectively.

The separation process is then stopped. After a cooling period the Ta container was taken away and the distribution of the radioisotopes ^{67}Ga and ^{65}Zn was measured before and after treatment of the various parts of the apparatus with solutions of 0.1 M HCl and 0.2 M HNO_3, respectively.

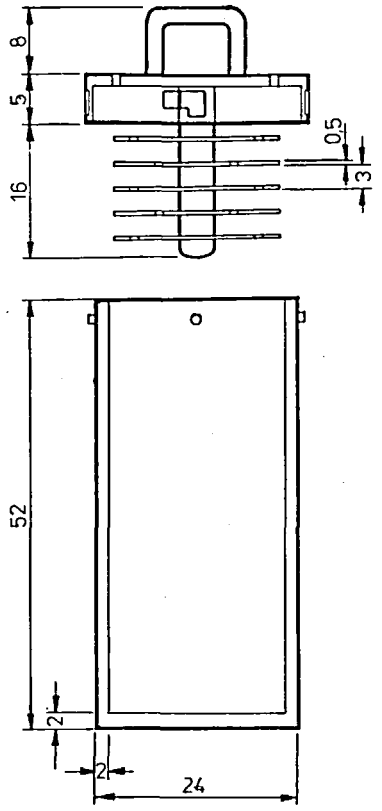

Fig. 4. Schematic view of a tantal container used in the separation experiments

Experimental conditions and results (in per cent of ^{67}Ga and zinc in the individual compartments) are summarized in Tab. 1.

The results of the thermochromatographic separation are discussed as follows:

Tab. 1. Separation efficiencies of ^{67}Ga and zinc using the Ta-container

temperature/period (two steps)	^{67}Ga (%)			zinc (%)
	in final solution	in zinc fraction	in tantal container	in final solution
720 K/150 min 820 K/ 60 min	94.03	5.58	0.4	0.0870
720 K/100 min 940 K/ 60 min	93.55	6.45	0.1	0.0116
780 K/100 min 1080 K/ 60 min	93.34	6.31	0.3	0.0118

1. At temperatures of $T > 900$ K yields of ^{67}Ga of about 93% were obtained. The rest of the radionuclide is released from the Ta container and is adsorbed on the quartz surface of the facility. The radioisotope is washed from the surface of the Ta container by diluted mineralic acids. Only minimum amounts of ^{67}Ga of $<0.4\%$ are detectable within the Ta container after purification with the mineralic acids.

It should be noted that these contaminations are concentrated at the lid of the container. The lid contains about 90%, the pot adsorbed only about 10% of the ^{67}Ga contaminations.

2. The zinc contamination of the final ^{67}Ga fraction are of the order of 10^{-2}% with respect to the original amount of the target.

3. Further purification of the ^{67}Ga fraction is possible by varying the parameters of the vacuum thermochromatographic separation process, i.e. heating temperatures higher than 1200 K and heating periods of several hours.

4. After a final and simple purification using ion exchange on DOWEX 1×8 the Zn contaminations of the ^{67}Ga solutions were reduced to a minimum undetectable by γ-spectroscopy. Fig. 5 offers the isotope composition of such a ^{67}Ga solution after the entire separation process. The sample was measured 33 days after the

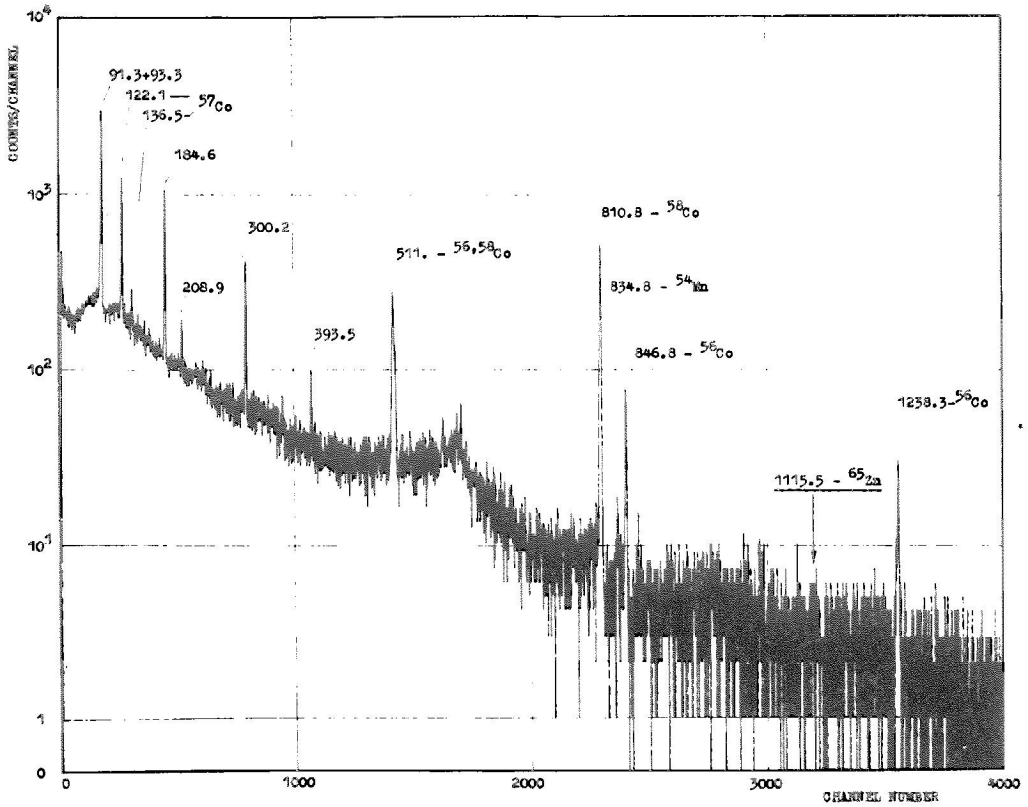

Fig. 5. γ-spectroscopic analysis of the final ^{67}Ga fraction thermochromatographic and ion exchange purification

separation. The ^{65}Zn is not detectable. Other contaminations were found to be ^{56,57,58}Co and ^{54}Mn ($5 \cdot 10^{-3}$% and $9 \cdot 10^{-5}$% of the activity of ^{67}Ga at EOB, respectively).

4. Discussion

The release of the target metal is in general similar to a distillation process. On the other hand, the release of the radioisotope ^{67}Ga can be characterized in terms of adsorption/desorption equilibria.

The results of the vacuum thermochromatographic experiments described here can be compared with other experimental data as well as with theoretical considerations. In particular, for theoretical considerations a model of "selective thermic desorption" (STD) was evaluated in [11].

The thermic desorption can be described by the parameters T_d (temperature of desorption of the components), t (period of desorption at a given temperature), ν_1 (kinetic constant of the desorption reaction) and $\Delta\bar{H}_a$ (differential enthalpy of adsorption) [10, 11].

The criteria of a successful realization of "STD"-separations are maximum differences ΔT_d between the desorption temperatures T_d of the two adsorptive metals, depending on the type of adsorbent metal applied.

Fig. 6 demonstrates the process (model) parameters of thermic desorption of carrier-free zinc and gallium with respect to tantal surfaces. Values of $\Delta T_d = 909$ K and 673 K for $\nu_1 = 10^8\ s^{-1}$ and $10^{12}\ s^{-1}$, reflect satisfactory separability of the combination by STD.

With respect to the desorption characteristic the experimental results of $t_{0.5} = 30\,(5)$ min at $T = 780$ K for zinc and of $t_{0.5} = 15\,(2)$ min at $T = 1370$ K for gallium coincide well with the calculated data, marked in Fig. 6 at $\nu_1 = 10^{12}\ s^{-1}$.

The differential molar (first) enthalpy of adsorption of zinc on tantal surfaces is small (-221.5 kJ · mole^{-1}, [10]). Consequently, no measurable differences between the temperature release of the target material zinc at absence or presence of a tantal foil were detected.

However, gallium is desorbed and adsorbed on quartz and several metallic surfaces at higher temperatures and quite differently. Experimental data are known for example for its thermic adsorption on quartz of $T_a = 833\,(30)$ K [12], on Cu and Ni of 935 (40) K and 1193 (20) K [13] in a H_2 atmosphere. These stronger interactions between adsorptive (^{67}Ga) and adsorbent (metallic surface) correspond to known values of the enthalpy of adsorption. The precise data are $\Delta\bar{H}_a = -350.0$ kJ · mole^{-1} (Ga on Cu) and -414.6 kJ × mole^{-1} (Ga on Ni) [10].

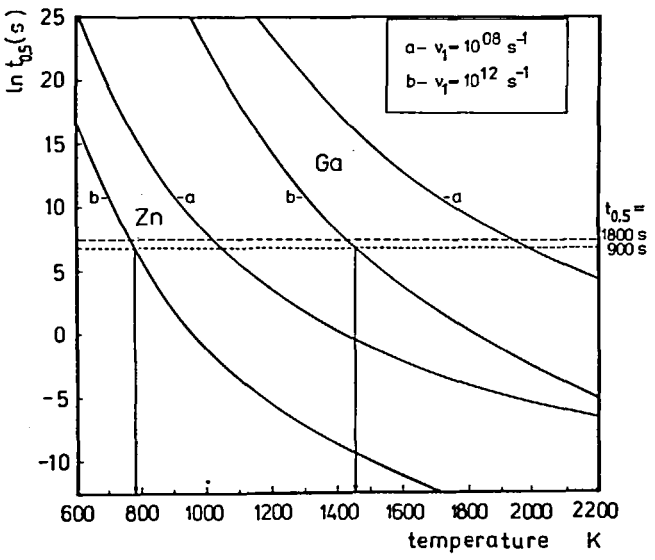

Fig. 6. Model parameter of selective thermic desorption separation processes of gallium and zinc with respect to tantal adsorbens surfaces

5. Conclusions

The quality of the separation processes of the types discussed is described by one or more of the following parameters:

- release (yield) of the radionuclide (in per cent or absolute specific activity),
- contamination of the radionuclide final fraction by the target material (with respect to the original amount of the target material) in per cent and/or absolutely (µg target material per unit specific volume radioactivity of the radioisotope),
- chemical and radiochemical purity of the final radioisotope fraction,
- technological parameters (separation time, costs, radiation hazard and others).

We do not wish to compare the different separation techniques known for ^{67}Ga separations from metallic zinc targets. Nevertheless, besides the separation efficiencies some advantes of the vacuum thermochromatographic separation are described. For example, simple regeneration of the enriched target metal is possible.

Theoretical considerations of the thermic adsorption/desorption behaviour of the metal pairs with respect to the metallic surface of the adsorbent were found to be useful to gain technologies for the desired separation problem.

The coincidence of the calculated and the experimental parameters of the thermic release of zinc and gallium from tantal surfaces is satisfactory. This should be pointed out, taking into account the model character of the calculations of T_d and $t_{0.5}$ as well as the derivations from the idealized state turning to real experimental conditions.

Received and accepted June 23, 1989

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